DEVELOPMENT OF CEMENT KILN DUST (CKD) BASED CATALYST FOR BIODIESEL PRODUCTION FROM WASTE COOKING OIL

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ABSTRACT

Cement kiln dust (CKD) is alkaline materials which produce as a by-side product in the cement manufacturing process which contain amount of alkalis like NA2O, K2O and large amount of free lime. The price of catalyst derived from noble metals such as platinum is expensive and this will drive the price of biodiesel even higher than the dinodiesel. Therefore, it is necessary to synthesize a cheaper catalyst to make the production of biodiesel competitive and feasible. In this work, CKD will be utilised as raw material to produce catalyst for transesterification of waste cooking oil. This CKD based catalyst was prepared by impregnated with the potassium hydroxide and the other by methanol and water. The catalyst was calcined at 650 °C for 3 hours. The transesterification process of waste cooking oil with methanol was used to investigate the yield of biodiesel. The catalysts were characterized using pH measurement, Thermogravimetric analysis (TGA) and Fourier transform infrared (FTIR). The experimental result showed that a CKD/KOH give the highest purity and yield of biodiesel compared to the other catalyst which is 97.85% and 89.34%. The higher alkalinity gives the higher purity and yield. This CK/KOH catalyst is the best catalyst compared to CKD, CKD/CH3OH and CKD/H2O for the biodiesel production. The catalyst can be produce with a low cost of material and high efficiency of production.

ABSTRAK

Habuk tanur simen (CKD) adalah bahan-bahan alkali yang menghasilkan sebagai produk sampingan dalam proses pembuatan simen yang mengandungi jumlah alkali seperti NA2O, K2O dan jumlah kapur yangbesar. Harga pemangkin yang berasal dari logam seperti platinum adalah mahal dan ini akan mendorong harga biodiesel lebih tinggi daripada dinodiesel. Oleh itu, keperluan untuk mensintesiskan satu pemangkin yang lebih murah untuk membuat pengeluaran biodiesel berdaya saing dan boleh dilaksanakan. Dalam kerja lapangan ini, CKD akan digunakan sebagai bahan mentah untuk menghasilkan pemangkin untuk transesterification sisa minyak masak. Ini pemangkin berasaskan CKD telah disediakan oleh impregnated dengan hidroksida kalium, methanol dan air. Pemangkin calcined pada suhu 650 ° C selama 3 jam. Proses transesterification sisa minyak masak dengan metanol telah digunakan untuk menyiasat hasil biodiesel. Pemangkin dicirikan menggunakan pengukuran pH, Thermogravimetric analisis (TGA) dan Fourier transform infrared (FTIR). Hasil uji kaji menunjukkan bahawa CKD / KOH memberikan ketulenan tertinggi dan hasil biodiesel berbanding pemangkin lain iaitu 97,85% dan 89,34%. Kealkalian yang tinggi memberikan ketulenan dan hasil yang lebih tinggi. Ini pemangkin CK/KOH adalah pemangkin terbaik berbanding dengan CKD, CKD/CH3OH dan CKD/H2O untuk pengeluaran biodiesel. Pemangkin ini boleh menghasilkan dengan kos bahan mentah yang rendah dan kecekapan pengeluaran yang tinggi.

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LIST OF SYMBOLS

%	Percentage
US $	United States Dollar
<	Less than
°C	Degree Celsius
µ	Micro

LIST OF ABBREVIATIONS

CKD	Cement Kiln Dust
cm	centimeter
cm^{-1}	per centimeter
FAEE	Fatty acid ethyl esters
FAME	Fatty Acid methyl esters
FT-IR	Fourier Transform Infrared Spectrometry
GC MS	Gas chromatography with a mass selective detector
h	hour
L	litre
mg	miligram
ml	mililiter
mm	milimeter
rpm	revolution per minutes
TGA	Thermogravimetric
U.S.	United States
USEPA	United States Environmental Pollution Agency
WCO	Waste cooking oil

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

Cement kiln dust (CKD) is alkaline materials which produce as a by-side product in the cement manufacturing process. CKD is a fine-grained solid and is a highly alkaline waste material that is removed from cement kiln exhaust gas. This material is consisting of fine particles gathered by dust collection system during the cement manufacturing process. (Mackie et al., 2009; Konsta-Gdoutos and Shah, 2003; Peethamparan et al., 2008).

In general, there are some elements in the CKD such as Ca, Fe and Sr. (Polat et al., 2004). All CKD mainly contains amount of alkalis (NA_2O, K_2O) and sulfate besides contain a large amount of free lime. Free lime in the CKD can make it a substitute for fertilizers and stabilizing wastewater streams (Konsta-Gdoutos and Shah, 2003).

In the recent survey in the United State showed, there are 87 million tonnes of cement clinker produced in 2006, 1.2 million tonnes of CKD were reused on or off-site (not including recycling into kiln feed) while 1.4 million tonnes were landfilled. In addition, 0.3 million tonnes of CKD was reclaimed from landfills, mainly for use as kiln feed (Mackie et al., 2009). The higher alkalinity and finer particle size in their properties make CKD usable for several applications such as waste solidification, replacement of

Portland cement in concrete block manufacturing, construction of hydraulic barriers (Peethamparan et al., 2008) also as a catalyst (Lin et al., 2011).

CKD has been found to be efficient, inexpensive and environmental friendly catalyst for biodiesel production (Lin et al., 2011). The combination of this CKD and WCO for biodiesel production makes it more inexpensive and worth. It is reported that approximately 70%-85% of the total biodiesel production cost arises from the cost of the raw material (Fatimah, 2009). WCO is easy to be found everywhere in the world, which have a large amount of waste lipids generated from restaurants, food processing industries and fast food shops everyday (Fatimah, 2009).

1.2 PROBLEM STATEMENT

There are a big number of wastes CKD in the United States that was researched by Mackie et al. (2010) which is about 87 millions of CKD was generated in 2006. Most of this waste reused as a soil or clay stabilization, agricultural soil amendment, concrete products and etc (Adaska et al., 2008).

CKD is also suitable used as a catalyst for biodiesel production which can improve the performance of biodiesel production (Lin et al., 2011). CKDs are widely available and typically available at no cost compared to other catalyst like platinum. It can be alternative as a catalyst. The component of CKD contains of silica, calcium carbonate, and calcium oxide “free lime” (Peethamparan et al., 2008) which is suitable as a catalyst to produce the biodiesel in the high performance of production.

Currently, the high cost of biodiesel is the major blockage for biodiesel to commercialize. Biodiesel usually costs over US$0.5/l, compared to US$0.35/l for petroleum based diesel. It is reported that the high cost of biodiesel is mainly due to the cost of virgin vegetable oil (Zhang et al., 2003).

The use of waste cooking oil replace the virgin oil to produce biodiesel is an effective way to reduce the raw material cost because it is estimated about half of the price of virgin oil. In addition, using waste cooking oil could also help to solve the problem of waste oil disposal (Zhang et al., 2003).

1.3 OBJECTIVE OF STUDY

The objective of this research is to develop a CKD based catalyst for biodiesel production from waste cooking oil (WCO) transesterification using various activation methods.

1.4 SCOPE OF RESEARCH

In order to achieve the objective of this research, which is to develop a CKD based catalyst for waste cooking oil (WCO) transesterification using various impregnation alkali solutions, the scope of study was divided into two main parts as following:

1. To characterize the CKD in term of pH of the catalyst with the pH meter, functional group of elements with Fourier Transform Infrared Spectrometry (FTIR) and the change in weight with the relation change in temperature using Thermogravimetric analysis (TGA).
2. To evaluate the catalyst performance using transesterification process of biodiesel from waste cooking oil.

1.5 RATIONAL AND SIGNIFICANT

The purpose of this study is to produce CKD waste as catalyst for biodiesel production from WCO. As knowing in the Adaska et al. (2008) mentioned that the CKD production was used as clay stabilization, agricultural soil amendment, concrete products and etc. The catalyst that have been used for biodiesel production before like glucose–

starch mixture (Chen et al., 2011) and metal oxide (Zabeti et al., 2009). The significant to produce CKD as a catalyst because it has low material cost compare to the other catalyst like platinum and etc because it get from the waste of cement production.

CHAPTER 2

LITERATURE REVIEW

2.1 CEMENT KILN DUST

2.1.1 Overview of cement kiln dust

Cement manufacturing is an important manufacturing throughout the world. United States plant produces 99.8 million metric tons of cement in 2006. Cement kiln dust (CKD) is a by-product material of the cement manufacturing process. The byproduct industrial and waste materials must be managed responsibly to ensure a clean and safe environment. Over the past several years, the management and uses of cement kiln dust was increasing dramatically, thus reducing its dependency on landfill disposal (Adaska et al., 2008).

Cement kiln dust is produced in the kiln during the production of cement clinker. The dust is a particulate mixture of some calcined and unreacted raw feed. All particulates are captured by the exhaust gases and then collected in particular matter control devices such as cyclones, bag houses and electrostatic precipitators (Adaska et al., 2008). Cement manufacturing process is shown in the **Figure 2.1**.

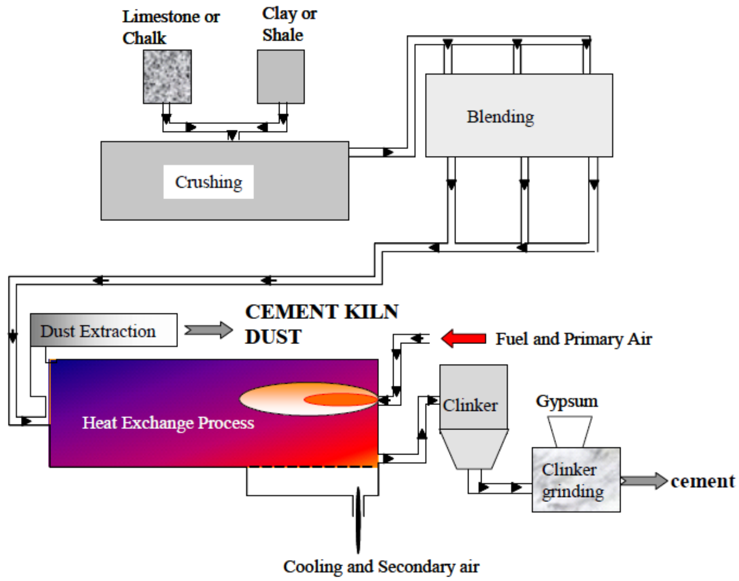

Figure 2.1: Cement manufacturing process (Sreekrishnavilasam and Santagata, 2006)

The chemical and composition content of CKD depends on the raw materials, plant configuration, and the processing type of cement production (Sreekrishnavilasam and Santagata, 2006). **Table 2.1** shows some typical composition of cement kiln dust in general.

Table 2.1: Typical composition of cement kiln dust by Haynes and Kramer (1982)

Constituent	% by weight	Constituent	% by weight
$CaCO_3$	55.5	Fe_2O_3	2.1
SiO_2	13.6	KCl	1.4
CaO	8.1	MgO	1.3
K_2SO_4	5.9	Na_2SO_4	1.3
$CaSO_4$	5.2	KF	0.4
Al_2O_3	4.5	Others	0.7

2.1.2 Cement Kiln dust disposal

Cement industry has established the Cement Manufacturing Sustainability (CMS) Program to balance society's need for cement products. The major element in the CMS programmed is to establish the Environmental Performance Measures. In the case of CKD in the U.S. cement industry, at year 2020, 60 percent reduction (from a 1990 baseline) in the amount of cement kiln dust disposed per ton of clinker produced (Sreekrishnavilasa and Santagata, 2006). **Figure 2.2** shows the flow chart for gross CKD management practices in the United States and **Table 2.2** shows the states with the Highest Amount of CKD Used for Beneficial applications and is currently developing a new CKD reduction goal (Adaska et al., 2008).

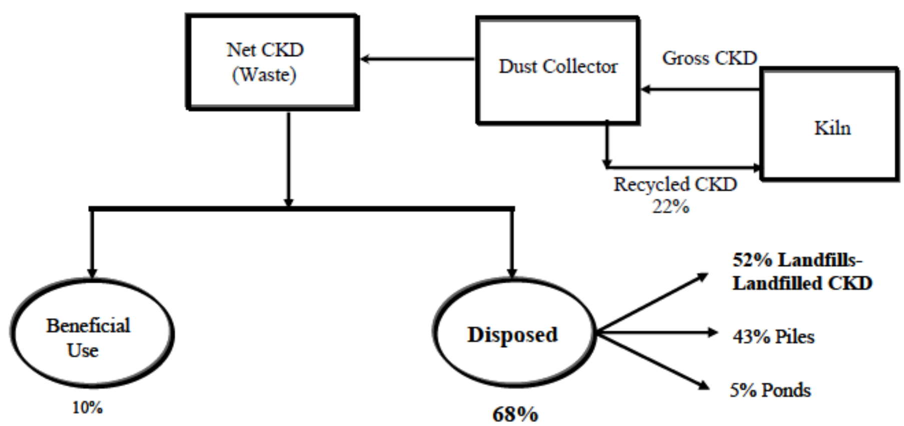

Figure 2.2: Flow chart for gross CKD management practices in the United States (Sreekrishnavilasam and Santagata, 2006)

In the United States more than four million tons of CKD that are unsuitable for recycling in the cement manufacturing process, require disposal annually. United States Environmental Pollution Agency (USEPA, 1993) estimated that, 52% was disposed in landfills, 43% percent in piles, and less than 5% in ponds. The average piles were 15 m thick. Maximum reported thickness for CKD landfills and waste piles were 56.4 m and 34.6m, respectively.

Table 2.2: The states with the Highest Amount of CKD Used for Beneficial applications

State	Quantity of CKD beneficially reused, metric tons	State	Quantity of CKD beneficially reused, metric tons
Oklahoma	154,477	Indiana	82,325
Texas	144,043	California	66,801
Pennsylvania	102,760	Arkansas	61,990
Ohio	86,453	Maryland	50,562
Illinois	85,330	Missouri	48,250

The amount of CKD used for beneficial applications has been increased dramatically over the 16 years. Annual use of CKD for beneficial applications has ranged from a low of 574,800 metric tons to 1.16 million metric tons. **Table 2.3** shows the historical cement kiln dust production and management (Adaska et al., 2008).

Table 2.3: Historical cement kiln dust production and management

Year	Plants responding to survey for given year	CKD beneficially reused on or off site, metric tons	CKD sent to landfill, metric tons	CKD reclaimed from landfilled, metric tons	Annual clinker production, metric tons	CKD sent to a landfill/clinker produced, kilograms / metric tons
1990	84	752,152	2,655,725	No data	44,360,364	60
1995	94	651,205	3,146,952	No data	61,729,315	51
1998	95	768,601	2,499,651	13,409	67,104,547	37
2000	92	574,803	2,223,190	79,171	68,263,086	33
2001	102	924,552	2,329,132	231,904	75,683,170	31
2002	101	664,848	1,989,680	103,223	77,636,598	26
2003	102	718,410	1,995,143	116,416	79,356,511	25
2004	102	917,968	1,993,421	69,099	83,945,430	24
2005	102	987,717	1,429,150	104,952	85,568,243	17
2006	101	1,160,011	1,403,062	261,351	86,686,834	16

2.2 CATALYST

A catalyst is a substance which changes the rate of a chemical reaction but is chemically unchanged at the end of the reaction. While most catalysts make the rate of chemical reactions go faster, but some can slow down the chemical rate. A catalyst can also make a chemical reaction possible that would not otherwise be.

Catalyst used in the transesterification of triglycerides can be classified as homogeneous and heterogeneous catalyst. Fatimah (2008) stated that excess amount of catalyst would lead to the higher amount of production cost and reduce the product yield.

2.1.1 Homogeneous Catalyst

Homogeneous catalyst is the process which involves at least one of the reactant. Basically, in this transesterification process, there are two types of homogeneous catalyst which is acid catalyst and alkali catalyst. Homogeneous basic catalyst provides much faster reaction rates than heterogeneous catalyst, but it is difficult to separate homogeneous catalyst from the reaction mixture (Fatimah, 2008).

2.1.2 Heterogeneous Catalyst

A heterogeneous catalytic is the process that involves more than one phase, usually the catalyst is a solid and the reactant and product are in liquid or gaseous form. There are many advantages of using heterogeneous catalyst such as non-corrosive, environmental friendly, fewer disposal problems, easier in separation from liquid product and they can be design to give higher activity, selectivity and longer catalyst lifetime. Example of heterogeneous catalyst such as alkaline earth metal oxides, anion exchange resins and various alkali metal compounds supported on alumina and that can be use in various type of chemical reaction including transesterification (Fatimah, 2008).

2.3 BIODIESEL

2.3.1 Background of Biodiesel

Biodiesel is known as an alternative diesel fuel especially for substitute diesel in developed countries mainly for transportation and agriculture industries. In recent years, biodiesel are more important due to insufficient of petroleum fuel and the needs of environmental friendly energy resources. Biodiesel is a renewable energy sources that are made from natural vegetable oil, animal fats, or singles cell oil (Ghadafi, 2008). However, the cost of biodiesel is high cause to the high cost of raw material (about 70-75% of the total cost) (Jasrina, 2008).

There are many ways how biodiesel roles of environment benefits more than fossil diesel. One of the key aspects of the life cycle assessment is a global warming potential, expressed as carbon dioxide, equivalent to CO2.CO2 is produced during the whole production process of fuels. According to the positive energy balance of biodiesel and the fact that biodiesel consists of renewable material one could expect a large saving of greenhouse gases compared to fossil fuel (Angela, 2009).

Nowadays, with the price of crude fossil fuel prices is too high, biodiesel have emerged as the fastest growing industries worldwide. Several countries especially United State and European Union are fully supporting the production of biodiesel from the agriculture sector. In year 2006, approximately 6.5 billion liters of biodiesel was produced globally. However, expected by the year 2020, biodiesel production from Brazil, China, India and some South East Asia countries such as Malaysia and Indonesia could contribute as much as 20% of production (Lam et al., 2010).

2.3.2 Composition of Biodiesel

Biodiesel is a mixture of fatty acid alkyl esters. There will be a mixture of fatty acid methyl esters (FAME) when methanol is used as reactant and if ethanol is used as reactant, the mixture will be fatty acid ethyl esters (FAEE). However, methanol is commonly used in biodiesel production because of their low cost and availability. Based on different feedstock, the biodiesel produced will have the different composition of FAME like in **Table 2.4** have shown below (Lam et al., 2010).

Table 2.4: Typical fatty acid composition (%) for different common oil source

Fatty acid	Soybean	Cottonseed	Palm	Lard	Tallow	Coconut
Lauric (C12:0)	0.1	0.1	0.1	0.1	0.1	46.5
Myristic (C14:0)	0.1	0.7	1.0	1.4	0.8	19.2
Palmitic (C16:0)	0.2	20.1	42.8	23.6	23.3	9.8
Stearic (C18:0)	3.7	2.6	4.5	14.2	19.4	3.0
Oleic (C18:1)	22.8	19.2	40.5	44.2	42.4	6.9
Linoleic (C18:2)	53.7	55.2	10.1	10.7	10.7	2.2
Linolenic (C18:3)	8.6	0.6	0.2	0.4	0.4	0.0

According to Lam et al. (2010) there are some of chemical structures of fatty acid methyl ester that will be found in the transesterification reaction of biodiesel production as shown in **Figure 2.5**.

Table 2.5: Chemical structure of common FAME

Methyl ester	Formula	Common acronym	Molecular weight
Methy palmitic	$C_{17}H_{34}O_2$	C16:0	270.46
Methy stearate	$C_{19}H_{38}O_2$	C18:0	298.51
Methy oleate	$C_{19}H_{36}O_2$	C18:1	296.50
Methy linoleate	$C_{19}H_{34}O_2$	C18:2	294.48
Methy linolenate	$C_{19}H_{24}O_2$	C18:3	292.46

2.4 TRANSESTERIFICATION PROCESS

Transesterification process is the process of converting vegetable & plant oil into biodiesel fuel. Chemically, transesterification means using a triglyceride molecule or a complex fatty acid and neutralizing the free fatty acids then removing the glycerin and will be creating an alcohol ester. The transesterification reaction is represented by the general equation as in the following equation 2.1. Transesterification is one of the reversible reactions and proceeds essentially by mixing with the reactants. The presence of a catalyst (a strong acid or alkali) will accelerate the conversion.

$$\text{Triglycerides} + \text{Methanol} \xrightleftharpoons{\text{Catalyst}} \text{Glycerol} + \text{Methyl Ester} \tag{2.1}$$

Transesterification of triglycerides with methanol and the presence of the catalyst will produce methyl ester and glycerol. The glycerol layer will be settles down at the bottom of the reaction vessel. In presence of excess alcohol, the forward reaction is first order reaction and the reverse reaction is found to be second order reaction. It was observed that transesterification is faster when catalyzed by alkali (Fatimah, 2008).

2.5 WASTE COOKING OIL

The raw material coming from waste vegetable oils or commonly known as waste cooking oils is one of the alternative sources. Waste cooking oil is easy to get from industries such as domestic usage and restaurant and also cheaper than other oils (refine oils) (Fatimah, 2008). Thus, neat vegetable oil is the best starting material compare to waste cooking oil because of the conversion of triackylglycerides to fatty acid methyl ester is high and the reaction time is relatively short. Waste cooking oil contains higher free fatty acid than neat vegetable oil (Ghadafi, 2008). Physical and chemical properties of waste cooking oil and palm oil can be shown in **Table 2.6**.

Table 2.6: Physical and chemical properties of used frying oil and neat palm oil (Ghadafi, 2008)

Property	UFO*	Neat Palm Oil
Acid value (mg KOH/g)	2.1	< 0.5
Kinematic viscosity at 40 °C (cSt)	35.3	30.2
Fatty acid composition (wt.%)		
Myristic (C14:0)	0.9	1
Palmitic (C16:0)	20.4	42.8
Stearic (C18:0)	4.8	4.5
Oleic (C18:1)	52.9	40.5
Linoleic (C18:2)	13.5	10.1
Linolenic (C18:3)	0.8	0.2
Others	6.7	0.9

* Sample has been pre-treated by filtering and dehydration before analysis.

As can be seen in the table, the waste cooking oil has properties much different from those from the neat oil. The advantages of using waste cooking oil are the low cost and prevention of environment pollution. Waste cooking oil need to be treat before dispose to the environment to prevent pollution. Due to the high cost of disposal, many people dispose waste cooking oil directly to the environment especially in rural area. Then, by recycling waste cooking oil will help to prevent pollution in the environment.

CHAPTER 3

METHODOLOGY

3.1 Introduction

This chapter mainly presents the materials and the experimental procedure of the characterization of cement kiln dust and transesterification process to produce biodiesel from waste cooking oil. There are three methods that have been used to characterize the catalyst which is to measure the pH value using Mettler Toledo pH meter, to know the functional group of the catalyst with Nicolet Avatar 370 DTGS Fourier Transform Infrared Spectrometry (FT-IR) and to measure the change in weight with the relation change in temperature using TGA Q500 Thermogravimetric analyzer (TGA). Biodiesel has been produced using transesterification process using waste cooking oil as a raw material. The presence of biodiesel then was detected by the Agilent Technologies 5975C Gas chromatography with a mass selective detector (GC MS).

3.2 MATERIALS

This section of raw materials was including the raw materials that have been used and the specific place obtained, chemicals and also all the equipment used throughout handling this research.